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# RETENTION OF $^{210}\text{Po}$ BY REFRACTORY OXIDES

W.H. HALE

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*Savannah River Laboratory*

*Aiken, South Carolina*

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# **RETENTION OF $^{210}\text{Po}$ BY REFRACTORY OXIDES**

by

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#### ABSTRACT

$^{210}\text{Po}$  is released from the refractory oxide barium cerate at 800-1000°C by a volume diffusion process.  $\text{BaCeO}_3$  is prepared by reacting  $\text{CeO}_2$  with  $\text{BaO}$  or  $\text{Ba}(\text{NO}_3)_2$  at 700°C, with  $\text{BaCO}_3$  at 800°C, or with  $\text{BaO}_2$  at 530°C.

## CONTENTS

	<u>Page</u>
INTRODUCTION . . . . .	5
SUMMARY . . . . .	6
DISCUSSION . . . . .	7
Selection of an Oxide Host Matrix . . . . .	7
Preparation of Barium Cerate and Barium Thorate . . . . .	10
Experimental Procedure . . . . .	10
Reaction of BaO with CeO <sub>2</sub> and ThO <sub>2</sub> . . . . .	11
Reaction of BaCO <sub>3</sub> with CeO <sub>2</sub> and ThO <sub>2</sub> . . . . .	12
Reaction of Ba(NO <sub>3</sub> ) <sub>2</sub> with CeO <sub>2</sub> . . . . .	14
Reaction of BaO <sub>2</sub> with CeO <sub>2</sub> . . . . .	16
Retention of Polonium by Oxide Matrices . . . . .	19
Pellet 1 . . . . .	20
Pellet 2 . . . . .	20
Pellet 3 . . . . .	20
Pellet 4 . . . . .	22
Pellet 5 . . . . .	24
REFERENCES . . . . .	27

## LIST OF TABLES AND FIGURES

<u>Table</u>		<u>Page</u>
I	Calculated Values of the Tolerance Factor for $ABO_3$ Perovskites . . . . .	9
II	Reactions of BaO with $CeO_2$ and $ThO_2$ . . .	11
III	X-ray Powder Patterns of $BaCeO_3$ and $BaThO_3$ . . . . .	12
IV	$^{210}Po$ Release from a $BaCeO_3$ Matrix at $900^\circ C$ . . . . .	21

<u>Figure</u>		
1	Classification of $A^{2+} B^{4+}O_3$ Compounds According to Ionic Radii . . . . .	7
2	Perovskite Crystal Structure of $A^{2+} B^{4+}O_3$ Compounds . . . . .	8
3	Thermograms of $BaCO_3$ - $CeO_2$ Reactions . . .	13
4	Thermograms of $Ba(NO_3)_2$ - $CeO_2$ Reactions and $Ba(NO_3)_2$ Decomposition . . . . .	15
5	Thermograms of $BaO_2$ - $CeO_2$ Reactions . . .	17
6	Differential Thermogram of $BaO_2$ - $CeO_2$ Reaction in Vacuum . . . . .	18
7	Release of $^{210}Po$ from Pellet of Barium Cerate . . . . .	21
8	Thermograms of $^{210}Po$ Release from a $BaO$ - $ThO_2$ - $PoO_2$ Pellet . . . . .	23
9	Thermogram of $^{210}Po$ Release from a $BaCeO_3$ Pellet . . . . .	24
10	Po-Pb Weight Loss from a $BaCeO_3$ Pellet at $965^\circ C$ . . . . .	26

## INTRODUCTION

$^{210}\text{Po}$  is a radionuclide with some of the properties that are required for application as an isotopic power source.  $^{210}\text{Po}$  has a high specific power and emits small amounts of penetrating radiation. The half-life of  $^{210}\text{Po}$  is 138.4 days; decay is by alpha emission (5.408 Mev) to stable  $^{206}\text{Pb}$ ; a 0.803 Mev gamma ray occurs in only  $1.07 \times 10^{-3}\%$  of the transitions. Pure  $^{210}\text{Po}$  has a specific power of 143 watts/g. However, because polonium metal melts at  $254^\circ\text{C}$  and has 1 atm vapor pressure at  $962^\circ\text{C}$ , it is unsuitable for high temperature applications.

A  $^{210}\text{Po}$  power source must be stable in air at  $1000^\circ\text{C}$  for use in a thermoelectric power converter. Gadolinium polonide, infused in tantalum rings, has been proposed as the heat source in some space missions; the polonide is stable at  $1000^\circ\text{C}$  and compatible with tantalum. However, it reacts vigorously with air at ambient temperatures to evolve finely divided  $\text{PoO}_2$ , and therefore could be hazardous if the containment capsule were breached. Polonium oxide, unlike lanthanide and actinide oxides, is volatile and, thus, not an acceptable fuel form.

Attempts to prepare refractory stoichiometric compounds of polonium were not successful.  $\text{BaPoO}_3$ , analogous to the refractory  $\text{BaTeO}_3$ , releases polonium at  $900^\circ\text{C}$ .  $\text{Ba}_3\text{PoO}_6$ , analogous to  $\text{Ba}_3\text{TeO}_6$ , could not be synthesized.

This report describes an attempt to stabilize  $\text{BaPoO}_3$  in dilute solid solution with a refractory oxide of similar structure. The synthesis and polonium retention characteristics of barium cerate ( $\text{BaCeO}_3$ ) and the synthesis of barium thorate ( $\text{BaThO}_3$ ), are also described.

### SUMMARY

$^{210}\text{Po}$  was not retained in refractory oxide matrices at 800-1000°C. Experiments were designed to place  $\text{BaPoO}_3$ , a perovskite-structure compound, in dilute solid solution with the perovskites,  $\text{BaCeO}_3$  and  $\text{BaThO}_3$ . Polonium was released from the  $\text{BaCeO}_3$  lattice by a volume diffusion process in which polonium diffuses slowly through either individual grains or the entire lattice.

Methods for synthesizing barium cerate and barium thorate were developed.  $\text{BaCeO}_3$  can be prepared by reacting  $\text{CeO}_2$  with  $\text{BaO}$  or  $\text{Ba}(\text{NO}_3)_2$  at 700°C, with  $\text{BaCO}_3$  at 800°C, or with  $\text{BaO}_2$  at 530°C.  $\text{BaThO}_3$  can be prepared by reacting  $\text{ThO}_2$  with  $\text{BaO}$  or  $\text{BaCO}_3$  at 900°C.



## DISCUSSION

Two binary oxides with the perovskite structure were selected as host lattices for  $^{210}\text{Po}$ . Methods were developed for synthesizing the perovskites at the lowest possible temperature, and the ability of the oxides to retain polonium was determined by calorimetry and thermogravimetric analysis.

### SELECTION OF AN OXIDE HOST MATRIX

A refractory binary oxide should contain  $\text{Po}^{4+}$ , the stable oxidation state at high temperature. Alkaline earth oxides are very stable and have high melting temperatures, and, in general, react with other metal oxides to form a refractory binary oxide. As shown in Figure 1,<sup>1</sup> the reaction of  $\text{BaO}$  with  $\text{PoO}_2$  should produce  $\text{BaPoO}_3$  with the cubic perovskite structure. Pure  $\text{BaPoO}_3$  has been prepared and shown to be volatile at  $900^\circ\text{C}$ .<sup>2</sup>

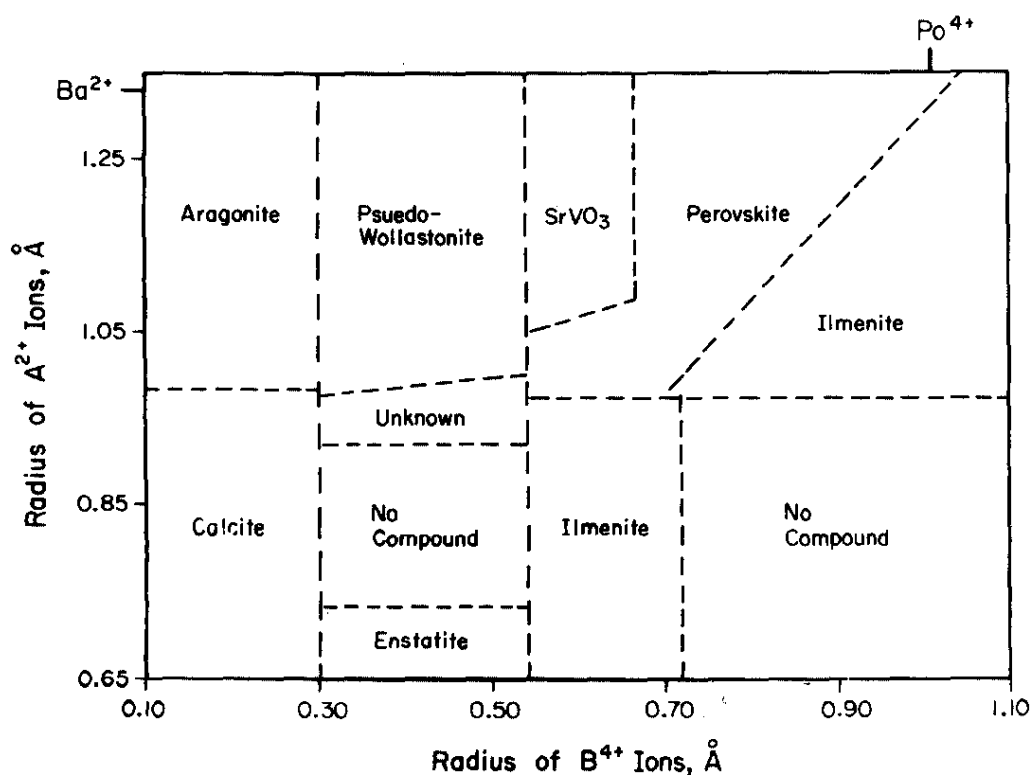


FIG. 1 CLASSIFICATION OF  $\text{A}^{2+} \text{B}^{4+}\text{O}_3$  COMPOUNDS ACCORDING TO IONIC RADII

The perovskite crystal structure of  $A^{2+}B^{4+}O_3$  compounds is shown in Figure 2. In the ideal cubic form of this structure, A has 12 oxygen neighbors. A polonium ion in the B position has 6 oxygen neighbors and should be resistant to further oxidation. A dilute solid solution of  $BaPoO_3$  in  $BaXO_3$  can be viewed as almost pure  $BaXO_3$  with a few  $X^{4+}$  ions replaced by  $Po^{4+}$  (a "substitutional" solid solution). Ideally,  $Po^{4+}$  ions would be trapped in this matrix, greatly reducing the volatility of  $^{210}Po$  at 900-1000°C.

Barium cerate and barium thorate satisfy the following criteria for maximum solubility with  $BaPoO_3$ :

- (1) The 4+ oxidation state of each element is stable at high temperature.
- (2) The ionic radii of  $Ce^{4+}$  and  $Th^{4+}$  are within 15% of that of  $Po^{4+}$ .
- (3) Both  $BaCeO_3$  and  $BaThO_3$  have the cubic perovskite structure.

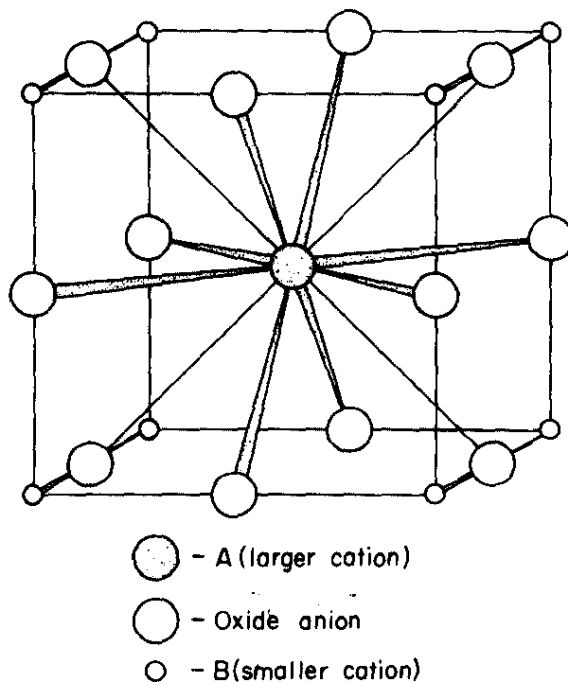


FIG. 2 PEROVSKITE CRYSTAL STRUCTURE OF  $A^{2+} B^{4+}O_3$  COMPOUNDS

Barium was the only alkaline earth used in this work. The divalent ions of the other alkaline earths are too small to form a cubic perovskite with  $\text{Po}^{4+}$ ,  $\text{Ce}^{4+}$ , or  $\text{Th}^{4+}$ . For an  $\text{ABO}_3$  perovskite, the ionic radii are related by<sup>3</sup>

$$r_A + r_O = t \sqrt{2} (r_B + r_O) \quad (1)$$

where:

$r_A$  = radius of the  $\text{A}^{2+}$  ion

$r_B$  = radius of the  $\text{B}^{4+}$  ion

$r_O$  = radius of the  $\text{O}^{2-}$  ion = 1.32 Å

$t$  = tolerance factor

Compounds with  $t$  between 0.80 and 1.00 usually have the perovskite structure. For lower values of  $t$  the ilmenite structure is found. The calculated values of  $t$  for several combinations of alkaline earths and the 4+ ions are given in Table I.

TABLE I

Calculated Values of the Tolerance  
Factor for  $\text{ABO}_3$  Perovskites  
(ionic radii in parentheses)

	Tolerance Factor (A/B)		
	$\text{Po}^{4+}$ (1.02 Å)	$\text{Th}^{4+}$ (1.02 Å)	$\text{Ce}^{4+}$ (0.94 Å)
$\text{Ba}^{2+}$ (1.34 Å)	0.80	0.80	0.83
$\text{Sr}^{2+}$ (1.12 Å)	0.74	0.74	0.76
$\text{Ca}^{2+}$ (0.99 Å)	0.70	0.70	0.72

Thus, barium is the only alkaline earth that can form a perovskite-structure compound with polonium, cerium, or thorium.

## PREPARATION OF BARIUM CERATE AND BARIUM THORATE

### Experimental Procedure

Barium cerate and thorate were prepared by reacting several barium reagents with  $\text{CeO}_2$  and  $\text{ThO}_2$ . Preliminary work indicated that  $\text{BaCeO}_3$  could be prepared at a lower temperature than  $\text{BaThO}_3$ , minimizing the potential for loss of  $^{210}\text{Po}$  during solid solution formation. Therefore, the synthesis of  $\text{BaCeO}_3$  was studied in greater detail.

$\text{CeO}_2$  and  $\text{ThO}_2$  were prepared by calcining the freshly prepared oxalates at  $600^\circ\text{C}$  for 5 hours. The sintered density of oxalate-produced  $\text{CeO}_2$  pellets was about 1.5 times greater than that of  $\text{CeO}_2$  pellets prepared by decomposing commercial cerous carbonate. The higher density indicates smaller particle size and thus a more reactive oxide. No difference in pellet density was observed between samples of thorium oxide obtained commercially and samples prepared by  $600^\circ\text{C}$  calcination of thorium oxalate or oxycarbonate.

The barium reagents were: (1) barium oxide, (2) barium carbonate (reagent grade), (3) barium nitrate (reagent grade), and (4) barium dioxide (technical grade).

In every case, reactants were mixed well, pelletized, and fired at the appropriate temperature. The powdered reactants (usually equimolar amounts) were mixed at high speed for 5 minutes in a Spex "Mixer/Mill,"\* Model 5000. About 10 mg of the mixed reactants were pressed into a pellet at 20 kpsi in a lubricated stainless steel die (0.19-in. diameter). Inclusion of 0.2 wt % polyethylene glycol binder strengthened the pellets. The pellets were placed on platinum plates and fired in air in either a tube or muffle furnace. For thermogravimetric analysis, pellet chips were placed in a platinum sample holder.

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\* Registered tradename of Spex Industries Inc.

Thermogravimetric data were obtained with an Ainsworth recording semimicro vacuum balance and a Marshall single-zone 1200°C tubular furnace. At a constant heating rate, both weight and the derivative of weight with respect to time were continuously recorded as a function of time. Evolved gases were determined with an in-line Associated Electronics Industries MS-10 mass spectrometer. A vacuum of  $10^{-6}$  -  $10^{-5}$  torr was obtained with a 300  $\ell$ /sec oil diffusion pump and a 425  $\ell$ /sec mechanical pump. Some data were also obtained with an R. L. Stone, TGA Model 5B system.

Reaction products were analyzed by X-ray diffraction. Chips of the fired pellets were ground and loaded into capillary tubes for powder pattern measurement. A standard lattice constant program<sup>4</sup> was used to calculate lattice constants from 2 $\theta$  values with the IBM 360 computer.

#### Reaction of BaO With CeO<sub>2</sub> and ThO<sub>2</sub>

Barium cerate was prepared by heating equimolar amounts of BaO with CeO<sub>2</sub> at 700°C for 16 hours; barium thorate was prepared at 900°C from BaO and ThO<sub>2</sub>. Pellets were fired in air at several different temperatures and the percentage reaction estimated from the X-ray powder pattern. These reactions cannot be studied by thermogravimetric analysis because no weight loss is involved.

TABLE II

Reactions of BaO with CeO<sub>2</sub> and ThO<sub>2</sub>

<u>Reactants</u>	<u>Time, hr</u>	<u>Temperature, °C</u>	<u>% Conversion to Product</u>
BaO-CeO <sub>2</sub>	16	600	0
	16	700	~98
	16	750	100
	16	800	100
	16	900	100
BaO-ThO <sub>2</sub>	16	700	0
	16	800	~10
	16	900	~95

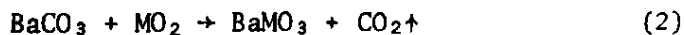
The products were identified by demonstrating that the interplanar spacings (d values) fit a cubic crystal system and by comparing the experimental lattice constants with those previously reported.<sup>1,5</sup> The data shown in Table III were averaged from six BaCeO<sub>3</sub> and five BaThO<sub>3</sub> products. The lattice constant of BaPoO<sub>3</sub> is 4.468 Å.

TABLE III  
X-Ray Powder Patterns of BaCeO<sub>3</sub> and BaThO<sub>3</sub>

Miller Index	BaCeO <sub>3</sub>		BaThO <sub>3</sub>	
	d, Å	Relative Intensity	d, Å	Relative Intensity
110	3.090	10	3.179	10
200	2.192	4	2.246	4
211	1.789	9	1.832	8
220	1.550	3	1.589	2
310	1.387	4	1.422	4
222	1.268	1	-	0
321	1.173	3	1.201	5
400	1.103	1	1.123	1
Lattice Constant, Å	4.410 ±0.003		4.511 ±0.004	
Previously Reported	4.387 <sup>1</sup>		4.48 <sup>5</sup>	

#### Reaction of BaCO<sub>3</sub> With CeO<sub>2</sub> and ThO<sub>2</sub>

Barium carbonate reacts with CeO<sub>2</sub> and ThO<sub>2</sub> with evolution of CO<sub>2</sub>.



Since pure BaCO<sub>3</sub> does not decompose below 1000°C, weight loss below 1000°C indicates that the reaction is occurring; the course of the reaction can be followed with thermogravimetric analysis. In preliminary work, pellets of BaCO<sub>3</sub>-CeO<sub>2</sub> and BaCO<sub>3</sub>-ThO<sub>2</sub> were fired in air for 16 hours. BaCeO<sub>3</sub> was formed at 850°C; BaThO<sub>3</sub>, at 900°C.

Thermograms of  $\text{BaCO}_3\text{-CeO}_2$  pellets showed a single weight loss period corresponding to  $\text{BaCeO}_3$  formation. When pellets were heated in static air at  $10^\circ\text{C/min}$ , reaction began at  $820^\circ\text{C}$  and was nearly complete at  $1080^\circ\text{C}$  (Figure 3). In vacuum, reaction began at  $800^\circ\text{C}$  and was only  $\sim 75\%$  complete at  $1080^\circ\text{C}$ . Because the reaction did not proceed faster in vacuum, diffusion of  $\text{CO}_2$  through either the entire pellet or individual grains must be the rate-determining process. Mass spectrometry confirmed that  $\text{CO}_2$  was evolved during the weight loss period. Activation energy for the reaction was 34 kcal/mole in vacuum and 26 in air.

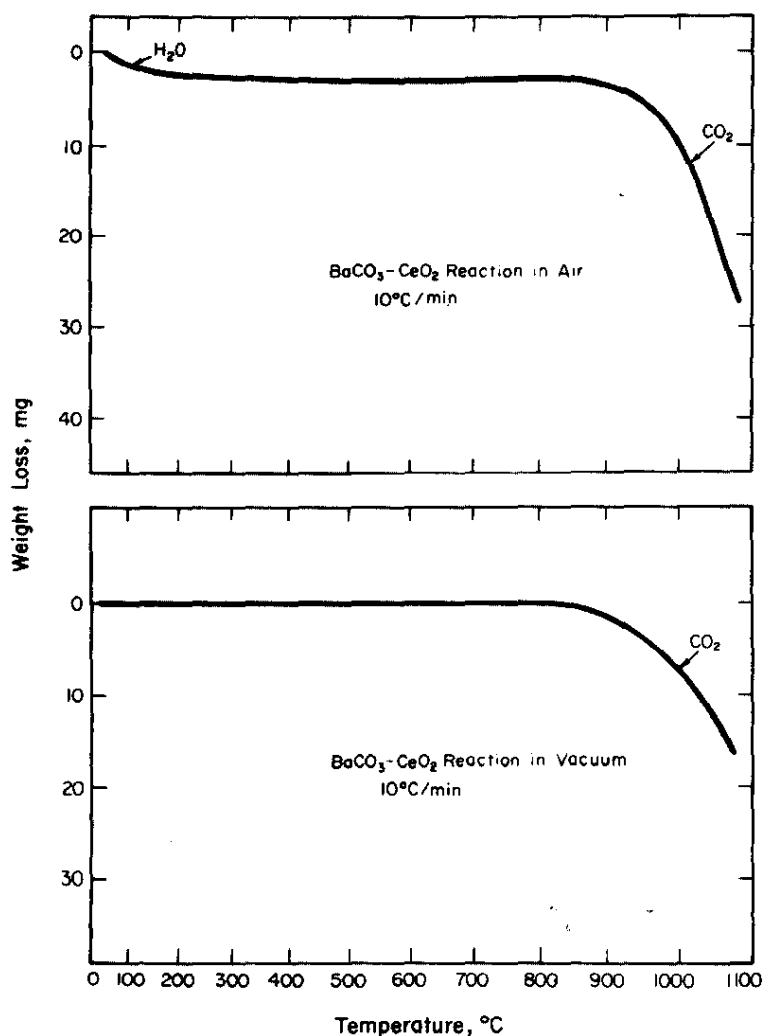


FIG. 3 THERMOGRAMS OF  $\text{BaCO}_3\text{-CeO}_2$  REACTIONS

### Reaction of $\text{Ba}(\text{NO}_3)_2$ With $\text{CeO}_2$

Barium nitrate decomposes to  $\text{BaO}$  which then reacts with  $\text{CeO}_2$ . Weight loss from a  $\text{Ba}(\text{NO}_3)_2$ - $\text{CeO}_2$  pellet, heated in static air at  $10^\circ\text{C}/\text{min}$ , began at  $550^\circ\text{C}$  and ended at  $830^\circ\text{C}$  (Figure 4). In vacuum, weight loss from a similar pellet began at  $500^\circ\text{C}$  and ended at  $800^\circ\text{C}$ . However, pure  $\text{Ba}(\text{NO}_3)_2$  also began to lose weight in vacuum at  $500^\circ\text{C}$ .

To determine if  $\text{BaCeO}_3$  was formed during the weight loss period,  $\text{Ba}(\text{NO}_3)_2$  -  $\text{CeO}_2$  pellets were fired in air for 18 hours at 600, 700, and  $800^\circ\text{C}$ . X-ray diffraction showed only traces of  $\text{BaCeO}_3$  produced at  $600^\circ\text{C}$  but complete formation at 700 and  $800^\circ\text{C}$ .



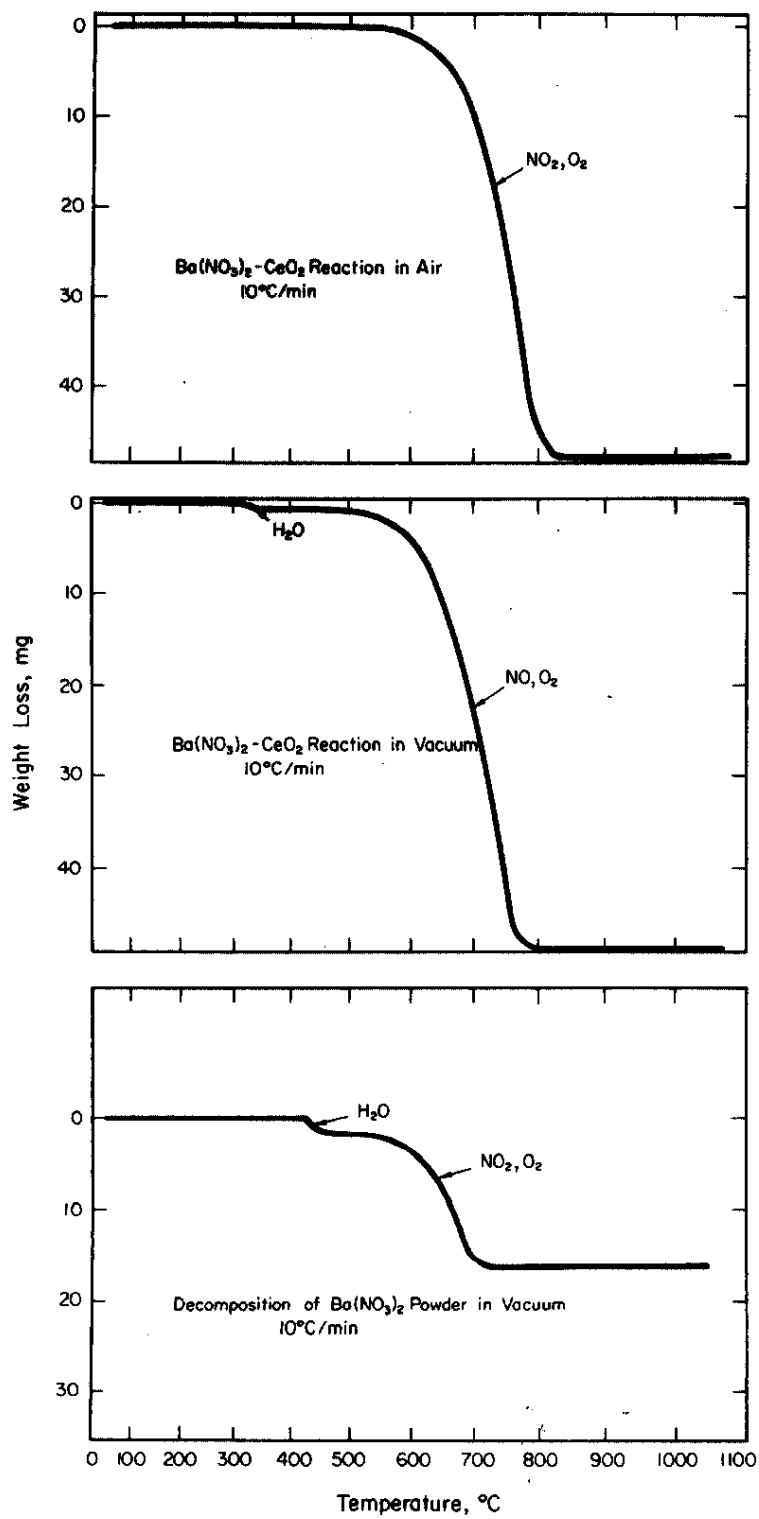
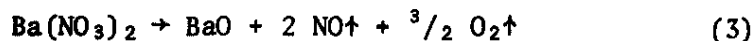


FIG. 4 THERMOGRAMS OF Ba(NO<sub>3</sub>)<sub>2</sub>-CeO<sub>2</sub> REACTIONS AND Ba(NO<sub>3</sub>)<sub>2</sub> DECOMPOSITION

Mass spectrometry at a pressure of  $2 \times 10^{-5}$  torr showed that NO and O<sub>2</sub> were evolved during the weight loss period, as shown in Equation 3.



In air, NO would be immediately oxidized to NO<sub>2</sub>. Activation energy for the Ba(NO<sub>3</sub>)<sub>2</sub>-CeO<sub>2</sub> reaction in vacuum was 31 kcal/mole.

#### Reaction of BaO<sub>2</sub> With CeO<sub>2</sub>

Thermograms of BaO<sub>2</sub>-CeO<sub>2</sub> pellets showed two distinct weight loss periods, the second one corresponding to BaCeO<sub>3</sub> formation according to Equation 4.



For pellets heated at 10°C/min in static air, the two reaction periods occurred at 25-320°C and 515-630°C (Figure 5). In vacuum, reaction temperatures were lowered to 25-200°C and 350-500°C. Pure BaO<sub>2</sub> showed no decomposition up to 750°C.

To determine which weight loss period corresponded to BaCeO<sub>3</sub> formation, BaO<sub>2</sub>-CeO<sub>2</sub> pellets were fired in air for 24 hours at several temperatures. No BaCeO<sub>3</sub> was formed at 250 and 400°C (first weight loss period in air); BaCeO<sub>3</sub> formation was complete at both 530 and 700°C (second period).

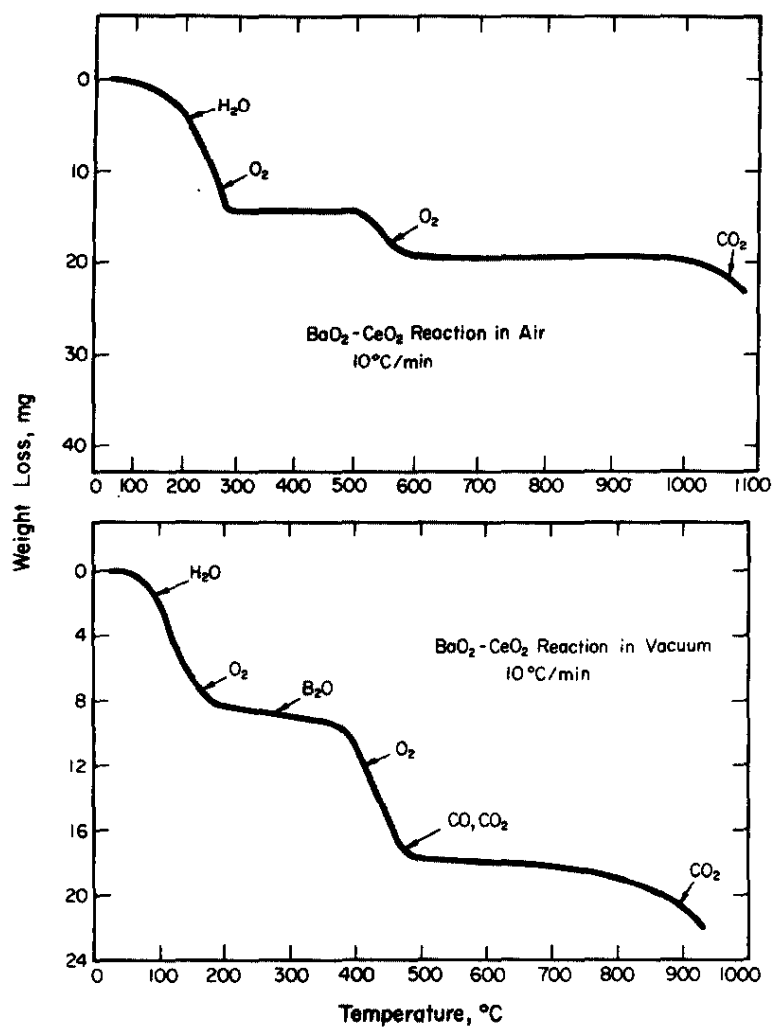


FIG. 5 THERMOGRAMS OF  $\text{BaO}_2\text{-CeO}_2$  REACTIONS

The complex differential thermogram (Figure 6) showed that each major weight loss period included at least two reactions. Mass spectrometry showed that  $\text{H}_2\text{O}$  was the primary species evolved in the first portion of the first weight loss period. The activation energy was 10 kcal/mole, a value typical of evolution of gaseous  $\text{H}_2\text{O}$  from pellets. The second portion of this period was evolution of  $\text{O}_2$ , possibly from the decomposition of  $\text{BaO}_4$ , a common impurity in technical-grade  $\text{BaO}_2$ . Activation energy for the first portions of the second weight loss period ( $\text{BaO}_2$ - $\text{CeO}_2$  reaction) was 34 kcal/mole.

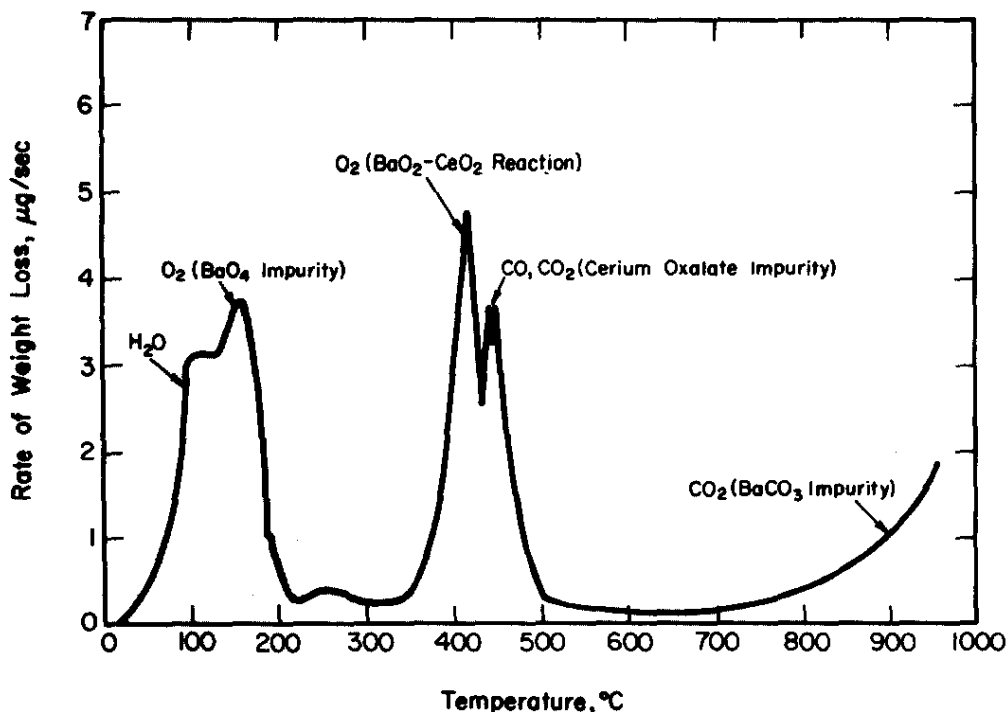


FIG. 6 DIFFERENTIAL THERMOGRAM OF  $\text{BaO}_2$ - $\text{CeO}_2$  REACTION IN VACUUM

The latter portion of this period was evolution of  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , probably from decomposition of residual cerium oxalate.  $\text{CO}_2$  was evolved during the high temperature weight loss period, indicating reaction of  $\text{CeO}_2$  with  $\text{BaCO}_3$  impurity.

## RETENTION OF POLONIUM BY OXIDE MATRICES

No conditions were found under which polonium could be retained in  $\text{BaCeO}_3$  or  $\text{BaO-ThO}_2\text{-PoO}_2$  matrices at  $1000^\circ\text{C}$ . In preliminary work, three Po-containing pellets were fired at various temperatures and analyzed for polonium retention and extent of reaction. Polonium retention characteristics of both matrices were determined more accurately when contained TGA equipment became available. One pellet of each matrix was studied with TGA.

$\text{BaCeO}_3$  can be prepared at  $700^\circ\text{C}$  in a  $\text{BaO-CeO}_2\text{-PoO}_2$  mixture without loss of polonium. However, polonium is released in the critical temperature range  $800\text{-}1000^\circ\text{C}$ . That the chemical form of polonium at this point could not be determined is not important for these reasons: (1) If  $\text{PoO}_2$  has not reacted at  $800^\circ\text{C}$ , it escapes from the lattice before the solid solution has been formed. (2) If the  $\text{BaCeO}_3\text{-BaPoO}_3$  solid solution exists at  $800^\circ\text{C}$ ,  $\text{BaPoO}_3$  decomposes upon subsequent heating and escapes from the lattice, probably as  $\text{PoO}_2$ . Because the temperature required to prepare  $\text{BaThO}_3$  is high,  $\text{PoO}_2$  escapes from the lattice before a solid solution can be formed.

Polonium-containing pellets were prepared by techniques similar to those described earlier.  $^{210}\text{Po}$  metal, deposited on platinum gauzes, was purchased from Mound Laboratory. Polonium was dissolved from the gauzes in concentrated  $\text{HNO}_3$  and precipitated as  $\text{Po(OH)}_4$  by the addition of concentrated  $\text{NH}_4\text{OH}$ . The solution was filtered through a fine-pore glass frit, and the hydroxide cake was rinsed with  $1\text{M NH}_4\text{OH}$ . The hydroxide was transferred to a platinum dish and allowed to stand overnight while  $\text{Po(OH)}_4$  was self-calcined to  $\text{PoO}_2$ .  $\text{PoO}_2$  was mixed with appropriate amounts of the barium and cerium or thorium reagents in the Spex "Mixer/Mill." The mixture was pressed into a pellet at 20 kpsi. Pellets were placed on platinum plates and fired in steel containers, or placed in platinum pans for TGA studies.

After the pellets were fired, the extent of reaction to  $\text{BaCeO}_3$  or  $\text{BaThO}_3$  was determined by X-ray diffraction analysis of the pellet surface. The pellet was rotated on a "Norelco"\* wide-range goniometer during measurement. Because polonium was present in small amounts, conversion of  $\text{PoO}_2$  to  $\text{BaPoO}_3$  could not be determined. Polonium content before and after firing was determined with a milliwatt twin-bridge calorimeter.

The pellets were analyzed by thermogravimetric analysis with the Ainsworth balance - MS-10 mass spectrometer system described earlier.

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\*Registered tradename of Philips Electronic Instruments.

### Pellet 1

Pellet 1 contained 0.674 mmole  $\text{BaCO}_3$ , 0.678 mmole  $\text{CeO}_2$ , and 0.057 mmole  $\text{PoO}_2$  (11.91 mg  $^{210}\text{Po}$ ). The pellet was fired in a tightly closed steel container at  $800^\circ\text{C}$  for 24 hours. A small container of  $\text{CaO}$  was placed next to the pellet to act as an absorber for  $\text{CO}_2$ , the reaction product.

The fired pellet contained 10-20%  $\text{BaCeO}_3$  and only 9.5% of the original  $^{210}\text{Po}$ . The  $\text{CaO}$  powder fluoresced orange, indicating at least partial sorption of  $^{210}\text{Po}$ . X-ray diffraction of the powder showed only  $\text{CaO}$ .  $\text{PoO}_2$ , with a vapor pressure of  $\sim 0.6$  torr at  $800^\circ\text{C}$ , volatilized from the pellet.

### Pellet 2

Pellet 2 contained 1.091 mmole  $\text{BaCO}_3$ , 0.993 mmole  $\text{ThO}_2$ , and 0.040 mmole  $\text{PoO}_2$  (8.48 mg of  $^{210}\text{Po}$ ). The pellet was fired in a tightly closed steel container at  $900^\circ\text{C}$  for 20 hours.

The fired pellet contained no  $\text{BaThO}_3$  and only 9.8% of the original  $^{210}\text{Po}$ . Most of the polonium was adsorbed on the steel vessel walls, which had a blue fluorescence. The vapor pressure of  $\text{PoO}_2$  is  $\sim 6$  torr at  $900^\circ\text{C}$ .

The formation of  $\text{BaThO}_3$  was probably prevented by the accumulation of  $\text{CO}_2$  reaction product. If the vessel remained tightly closed, and all  $\text{BaCO}_3$  reacted, the partial pressure of  $\text{CO}_2$  would be  $\sim 7$  atm.

### Pellet 3

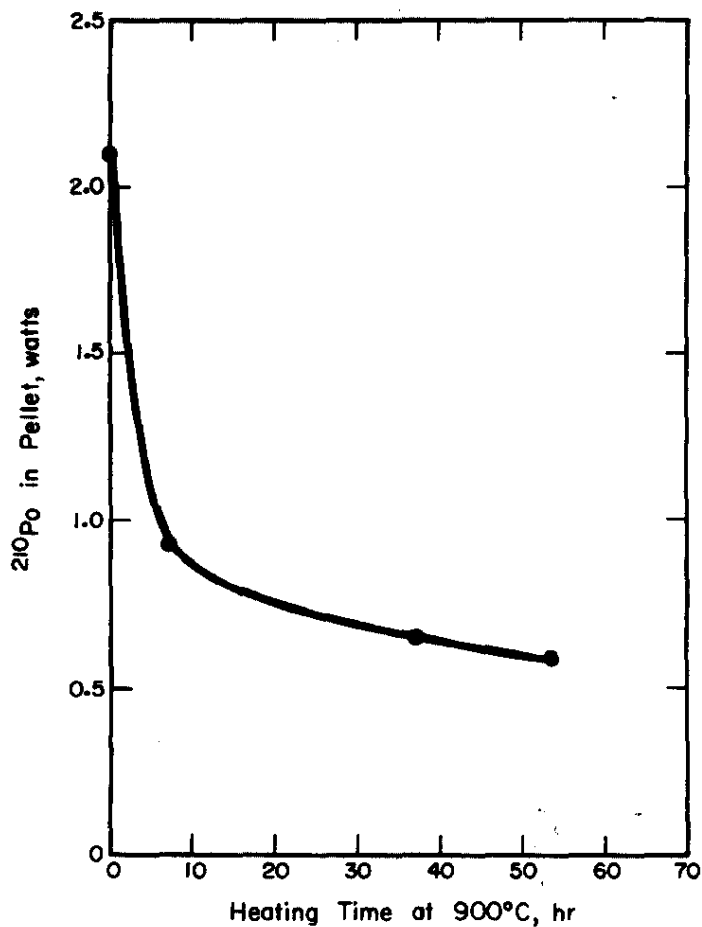
Pellet 3 contained 1.233 mmole  $\text{BaCO}_3$ , 1.134 mmole  $\text{CeO}_2$ , and 0.089 mmole  $\text{PoO}_2$  (18.6 mg  $^{210}\text{Po}$ ). The pellet was fired at  $850^\circ\text{C}$  for 18 hours in a steel container. The container had a loose fitting top to allow  $\text{CO}_2$  to escape but minimize the release of  $^{210}\text{Po}$  into the gloved box. The fired pellet contained  $\sim 70\%$   $\text{BaCeO}_3$  and 79% of the original  $^{210}\text{Po}$ .

As a test of the thermal stability of the  $^{210}\text{Po}$  solid solution, the fired pellet was heated to  $900^\circ\text{C}$  in a platinum boat inside a capped steel pipe. Both ends of the pipe protruded from the furnace to provide a cold trap for any polonium evolved from the pellet. As shown in Table IV and Figure 7, 72% of the  $^{210}\text{Po}$  was evolved at a decreasing rate. The power density decreased from 23.4 to 6.6 watts/ $\text{cm}^3$  at a mass density of  $4.4 \text{ g/cm}^3$  (about half the theoretical density of crystalline barium cerate).

TABLE IV

 $^{210}\text{Po}$  Release from a  $\text{BaCeO}_3$  Matrix at  $900^\circ\text{C}$ 

<u>Time at <math>900^\circ\text{C}</math>, hr</u>	<u><math>^{210}\text{Po}</math>, watts</u>	<u>% of original <math>^{210}\text{Po}</math> remaining in pellet</u>
0	2.097	100
7	0.925	44.1
37	0.647	30.9
53	0.586	27.9

FIG. 7 RELEASE OF  $^{210}\text{Po}$  FROM PELLETS OF BARIUM CERATE

#### Pellet 4

At the time Pellet 4 was prepared, it contained 0.571 mmole BaO, 0.524 mmole ThO<sub>2</sub>, and 0.063 mmole PoO<sub>2</sub> (13.2 mg <sup>210</sup>Po). 87% of the <sup>210</sup>Po had decayed to <sup>206</sup>Pb when polonium release was studied by TGA.

The purpose of this test was to analyze the polonium retention characteristics of a BaO-ThO<sub>2</sub>-PoO<sub>2</sub> mixture under the adverse conditions of vacuum and high rate of heating and to compare the data with a BaCeO<sub>3</sub>-BaPoO<sub>3</sub> mixture heated under favorable conditions (Pellet 5). To permit mass spectrometry, pellet 4 was heated in vacuum ( $\sim 10^{-5}$  torr) rather than the favorable oxygen atmosphere; the heating rate was 3°C/min, and reaction of the oxides to the perovskite compounds was probably incomplete.

The ordinary and differential thermograms are shown in Figure 8. H<sub>2</sub>O and CO<sub>2</sub> (from BaCO<sub>3</sub> impurity) were identified by mass spectrometry. Activation energies for the release of H<sub>2</sub>O and CO<sub>2</sub> were 8.4 and 34.2 kcal/mole, respectively. These values agree closely with data obtained in the earlier work with BaO<sub>2</sub>-CeO<sub>2</sub> and BaCO<sub>3</sub>-CeO<sub>2</sub> pellets.

The Po and Pb portions of the weight loss curve were assigned according to the known Po/Pb ratio. No ions corresponding to doubly charged Po or Pb species were observed in the mass spectrum (the spectrometer is limited to m/e ratios  $\leq 200$ ). Release of <sup>210</sup>Po was observed at  $\sim 850^\circ\text{C}$  with an activation energy of 39.0 kcal/mole. The initial release temperature was probably lower, but was obscured in the CO<sub>2</sub> weight loss. Evolution of lead began at  $\sim 960^\circ\text{C}$ . The temperature was maintained at 960°C until constant weight was attained. After this experiment, the quartz tube surrounding the sample holder had an intense violet fluorescence, confirming that <sup>210</sup>Po had been released.



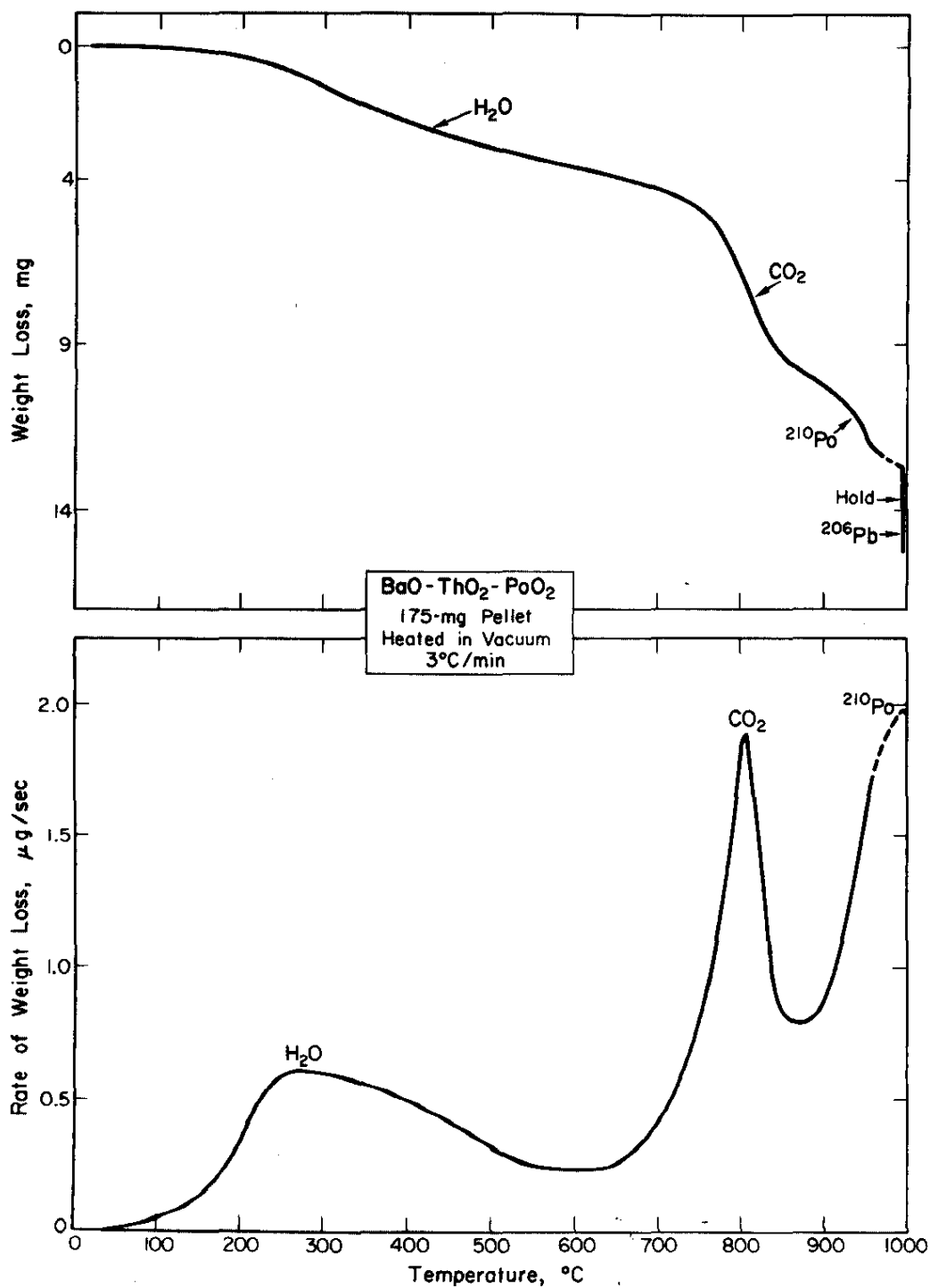


FIG. 8 THERMOGRAMS OF  $^{210}Po$  RELEASE FROM A  $BaO-ThO_2-PoO_2$  PELLETT

### Pellet 5

At the time Pellet 5 was prepared, it contained 0.571 mmole BaO, 0.524 mmole CeO<sub>2</sub>, and 0.031 mmole PoO<sub>2</sub> (6.45 mg <sup>210</sup>Po). 87% of the <sup>210</sup>Po had decayed when the thermogravimetric analysis was made.

The solid solution was prepared by heating the pellet to 700°C at 3°C/min in a flowing stream of 20% oxygen - 80% helium (thermogram shown in Figure 9). The temperature was maintained at 700°C for 20 hours. As shown earlier, these conditions are sufficient for reaction of the oxides to form BaCeO<sub>3</sub> and BaPbO<sub>3</sub>.<sup>9</sup> A minimum temperature for formation of BaPoO<sub>3</sub> has not been determined.

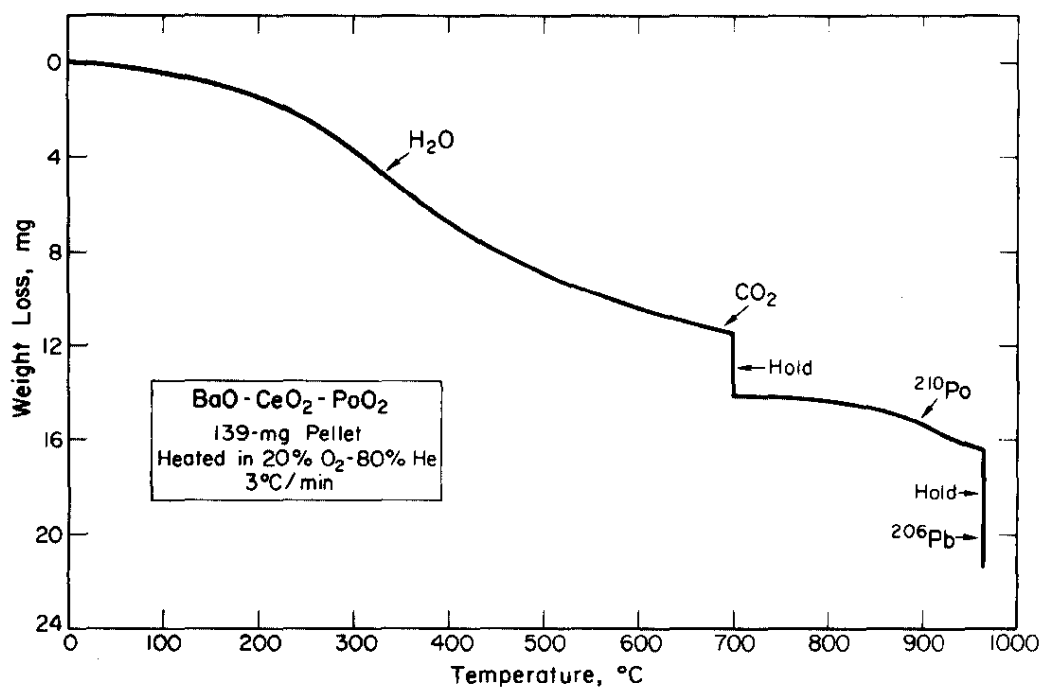


FIG. 9 THERMOGRAM OF <sup>210</sup>Po RELEASE FROM A BaCeO<sub>3</sub> PELLET

By analogy with Pellet 4, the first two weight loss periods were assigned to H<sub>2</sub>O and CO<sub>2</sub>. The pellet attained a constant weight during the 20-hour heating period indicating complete removal of H<sub>2</sub>O and CO<sub>2</sub>. No fluorescence was observed in the quartz tube after this heating period.

<sup>210</sup>Po release began at ~800°C with an activation energy of 45 kcal/mole, significantly higher than from the BaO-ThO<sub>2</sub>-PoO<sub>2</sub> pellet. <sup>206</sup>Pb release began at ~910°C with an activation energy of 50 kcal/mole. The lead release gave 82% of the high temperature weight loss compared to the theoretical 87%. <sup>210</sup>Po release was again confirmed by violet fluorescence in the quartz tube.

Release of Po and Pb from the pellet occurred by a volume diffusion process, as determined by holding the temperature constant at 965°C and determining the functional dependence of weight loss with time.<sup>7</sup> The data were fitted to an equation of the form

$$W = Kt^{1/2}$$

where

W = weight loss, mg

K = rate constant = 0.71 mg/min<sup>1/2</sup>

t = time, min

Since weight was lost before the constant temperature was reached and an arbitrary time zero could not be chosen, trial plots of weight loss versus the logarithm of time were made until a linear dependence with slope 1/2 was found. The resulting plot of the weight loss data using the time zero obtained in the trial plots is shown in Figure 10. Volume diffusion is the rate limiting process through 76% of the weight loss period; weight loss then becomes linear with time indicating that vaporization within the pellet is rate limiting.<sup>7</sup>

A volume-diffusion process can arise from two mechanisms, diffusion across a thickening depleted layer in the pellet or diffusion across layers in individual grains followed by rapid pore diffusion throughout the pellet. More experiments would be needed to determine the mechanism in this case.

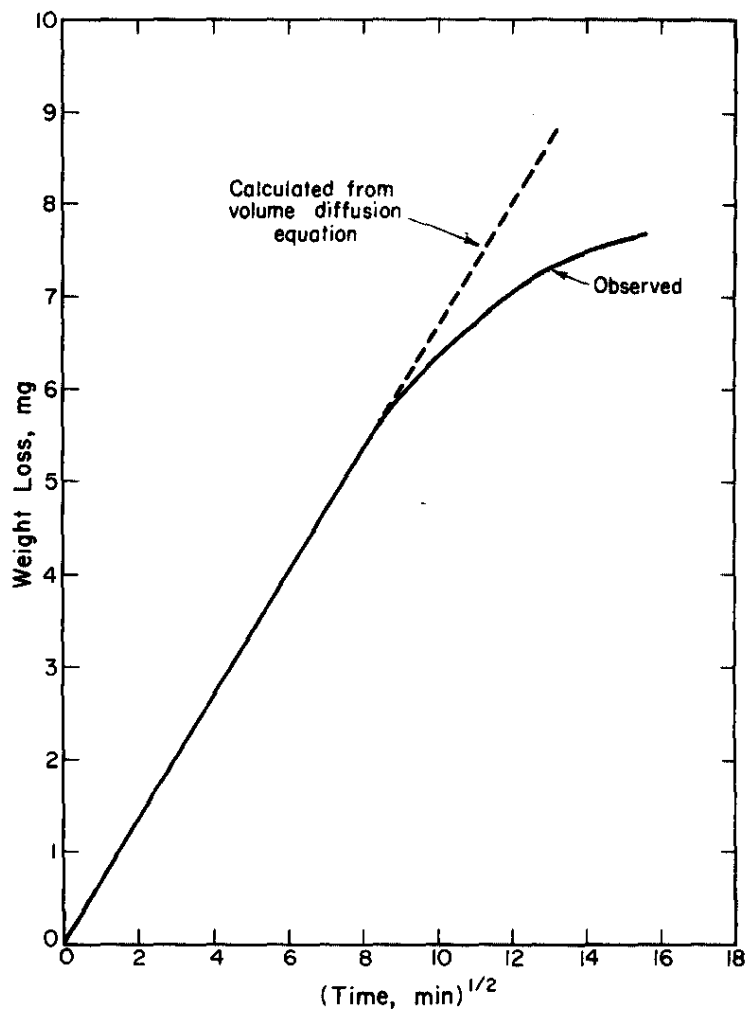


FIG. 10 Po-Pb WEIGHT LOSS FROM A  $\text{BaCeO}_3$  PELLET AT  $965^\circ\text{C}$

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